



Study of DPNR catalysts for combined soot oxidation and NO_x reduction

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ABSTRACT

The behavior of a model PtBa/Al₂O₃ model NSR catalyst in both the NO_x storage/reduction and soot oxidation is investigated in this work. It is found that the presence of soot negatively influences the NO_x storage capacity of the catalyst, evaluated at 623 K in presence of water and CO₂ in the feed stream: in fact the amounts of NO_x stored in presence of soot decrease by nearly 30% in the presence of roughly 10% (w/w) of soot. The presence of soot has a destabilizing effect on the NO_x adsorbed species, which decompose to a large extent in the absence of gas phase NO and oxygen. This has also been confirmed by dedicated TPD and TPO experiments. However the presence of soot does not appreciably affect the behavior of the PtBa/Al₂O₃ catalyst in the reduction by H₂ of the stored nitrates, being in all cases N₂ the major reaction product along with minor amounts of ammonia.

During the storage of NO_x, soot oxidation takes place. Notably, the stored NO_x participate in the soot oxidation upon release of NO₂ and O₂ which actively oxidize soot. However a direct participation of the adsorbed NO_x species in the oxidation of soot cannot be excluded.

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1. Introduction

Current and upcoming environmental legislations in the most developed countries are imposing severe limits in NO_x, hydrocarbon, CO and particulate (soot) emissions from diesel engines. While the control of soot emissions is currently accomplished by the use of the so-called diesel particulate filters (DPFs), suitable technologies for NO_x abatement in lean-burn engines are still under development [1]. Among these, lean NO_x traps (LNTs), also known as NO_x storage–reduction (NSR) systems, have been proposed. The NSR technique utilizes an unsteady state operation by switching between fuel-lean and fuel-rich conditions [2,3]. Standard NSR catalysts consist of precious metals and alkaline/alkaline-earth metal oxides, typically platinum and barium, respectively, dispersed on metal oxide supports such as alumina. During fuel-lean periods, NO_x are stored on the alkaline/alkaline-earth metal oxide; the stored NO_x are then reduced to N₂ during a short fuel-rich period [3].

To accomplish soot and NO_x removal, both de-soot and deNO_x after-treatment techniques must be used. In the late 1990, Toyota has developed a new technology able to remove simultaneously NO_x and soot [4,5]. This system, called diesel particulate–NO_x reduction (DPNR), consists of a porous ceramic filter coated with a catalytic layer consisting of a NSR catalyst. Like the NSR technology, this system accomplishes the reduction of soot and NO_x under

cyclic conditions: soot abatement occurs under lean conditions thanks to the presence of NO_x and the excess oxygen in the exhaust gas, but it is claimed to occur during the rich phase as well.

In previous works of our group the potentiality of a model PtBa/Al₂O₃ catalyst in the simultaneous removal of soot and NO_x has been investigated. It has been found that the PtBa/Al₂O₃ sample is able to oxidize soot in the presence of oxygen at temperatures above 623–673 K; the presence of NO in the gas phase significantly enhances the soot combustion activity [6,7], due to NO oxidation to NO₂ on Pt followed by the reaction of NO₂ with soot:



In reaction (1), CO₂ formation is envisaged but CO formation may occur as well. It is indeed well-known that NO₂ is a better oxidant than O₂ ([8] and references herein reported); its reaction with the carbonaceous material leads to both CO and CO₂ formation [8].

Based on a comparative study of a PtBa/Al₂O₃ catalyst with a Pt/Al₂O₃ sample, a role of the stored NO_x species in the oxidation of soot has been suggested [9]. In a recent paper by Kustov and Makkee [10] the soot oxidation on a number of alkaline-earth-based catalytic systems pre-saturated with NO_x, like Ba(NO₃)₂/Al₂O₃, has been investigated. The authors show that stored nitrates contribute to the soot oxidation by lowering the temperature of soot oxidation. Along similar lines, Suzuki and Matsumoto [11] noted an increased combustion activity of soot when a NO_x trap material is incorporated in the catalyst. On the other hand, Sullivan et al. [12] reported that the presence of a NO_x trapping component like BaO does not promote *per-se* the particulate combustion. However the

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NO_x trapping material promotes soot combustion due to the periodic localized increases in the NO₂ gas phase concentration during trap regeneration. On these bases, aim of this work was to provide new insights on the role in the soot combustion of NO_x stored onto the catalytic surface of a model PtBa/Al₂O₃ DPNR catalyst. Besides, we wanted to analyze the effects of the presence of soot on the behavior of the LNT catalyst in terms of NO_x storage/reduction. For this purpose, NO_x storage/reduction experiments have been performed over a model PtBa/Al₂O₃ catalyst by alternating lean/rich cycles both in presence and in absence of soot. The interaction between soot and the stored NO_x species has also investigated by temperature programmed methods under inert flow (TPD) or in oxygen (TPO) during which the stability/reactivity of the stored NO_x species has been analyzed both in the presence and in the absence of soot.

2. Experimental

The model catalyst studied, PtBa/Al₂O₃ (Pt loading near 0.8% (w/w) and Ba loading near 17% (w/w)), was prepared by the wetness impregnation technique from solutions of dinitrodiammine platinum (Strem Chemicals) and barium acetate (Strem Chemicals, as reported elsewhere) [6,13]. The catalyst presents a surface area near 160 m²/g_{cat} and pore volume of 0.8 cm³/g_{cat} (as determined by N₂ adsorption–desorption with a Micromeritics TriStar 3000 Instrument). The Pt dispersion is close to 15% (H₂ chemisorption at 273 K, measured with a TPD/R/O 1100 Thermo Fischer Instrument). Further details of catalyst preparation and characterization are reported in Refs. [14–16].

Printex-U (Degussa) was used as model soot [17,18]. Catalyst–soot mixtures were prepared by gently mixing in a vial the catalyst powder with the soot for 24 h, thus realizing a loose contact. A catalyst/soot ratio of 9/1 (w/w) was typically utilized in reactivity tests.

All reactivity tests were performed in a flow-reactor apparatus consisting of a quartz tube reactor (7 mm i.d.) connected to a mass spectrometer (Omnistar 200, Pfeiffer Vacuum) and to a microGC (Agilent 3000A) for the on-line analysis of the outlet gases [19]. The outlet NO, NO₂, NH₃ concentrations were also detected by a UV analyzer (Limas 11HW, ABB). 66 mg of the soot–catalyst (74–105 μm) mixture was used in each run, and the total gas flow was always set at 100 cm³/min (at 273 K and 1 atm).

Before catalytic tests, the catalyst/soot mixture has been heated at 773 K in He to remove any adsorbed species on the catalytic surface. The NO_x storage and reduction activity of the catalytic system has been studied in the presence and in the absence of soot by performing lean-rich cycles at constant temperature (Isothermal Step Concentration experiments, ISC). During the NO_x adsorption (lean phase, see Table 1), a pulse of NO (1000 ppm) has been admitted to the reactor in flowing He + 3% (v/v) O₂ until catalyst saturation. Then after a He purge at the same temperature, catalyst regeneration (rich phase, see Table 1) has been carried out with H₂ (4000 ppm in

He). The catalyst samples have been conditioned by performing few adsorption/regeneration cycles: conditioning lasted until a reproducible behavior has been obtained, and this typically required 2–3 cycles. 1% (v/v) H₂O and 0.1% (v/v) CO₂ were always present in the feed flow during both the storage and the reduction phase (Table 1). The CO₂ concentration is lower than real applications, but it is anyway representative of carbon dioxide effect on the catalytic system performance [16]. Besides such low value allows to appreciate even small changes in the CO₂ concentration during the experiments.

The selectivity to N₂ of the reduction process has also been estimated. Since the N₂ selectivity changes during the rich phase due to the variation in the product distribution with time, a time-weighted average N₂ selectivity (S_{N_2}) along the entire rich step has been estimated:

$$S_{N_2} = \frac{2n_{N_2}}{2n_{N_2} + n_{NO} + n_{NH_3}} \quad (a)$$

In Eq. (a) n_{N_2} , n_{NO} and n_{NH_3} are the total molar amounts of N₂, NO, and NH₃, respectively, evolved during the entire reduction phase. These amounts are obtained by the integrals on time of the concentrations of the products evolved during the entire reduction phase. N₂O has not been considered in Eq. (a) since formation of this species has been found to be negligible.

The thermal stability of the stored NO_x was analyzed by thermal decomposition in inert flow (temperature programmed desorption, TPD). After NO_x adsorption at 623 K the sample was cooled in He at 523 K and then heated (10 K/min) in He + H₂O (1%, v/v) and CO₂ (0.1%, v/v) from 523 K up to 773 K (hold 30 min) (see Table 1). These experiments have been carried out in the presence and in the absence of soot to analyze the effect of soot on the thermal stability of the adsorbed nitrates.

Finally, the behavior of the catalyst in the soot combustion reaction was investigated by means of temperature programmed oxidation (TPO). Like TPD experiments, after NO_x adsorption at 623 K the catalyst was cooled in He down to 523 K and then heated (10 K/min) in He + O₂ (3%, v/v) + H₂O (1%) + CO₂ (0.1%, v/v) from 523 K up to 773 K (see Table 1). These experiments have been carried out in the presence and in the absence of stored NO_x.

Soot is progressively consuming during each test; accordingly several catalyst/soot batches have been used. All the experiments refer to a soot loading near 7–8% of the catalyst weight.

3. Results and discussion

3.1. NO_x adsorption phase

The results obtained in the case of a rectangular step feed of NO (1000 ppm) in the presence of O₂ (3%, v/v), CO₂ (0.1%, v/v) and H₂O (1%, v/v) at 623 K carried out on the PtBa/Al₂O₃ catalysts in the absence and in the presence of soot (soot loading near 8% of the catalyst weight) are shown in Fig. 1A and C, respectively. The outlet NO, NO₂ and NO_x (NO + NO₂) concentration curves are displayed in the figure as a function of time, along with that of the NO inlet concentration (dotted lines). In the absence of soot (Fig. 1A), upon the NO step addition (at $t = 0$ s) the NO outlet concentration increases with time, approaching the asymptotic values corresponding to the NO inlet concentration after about 2000 s. Also NO₂ (140 ppm at steady-state) is observed due to the occurrence of the oxidation of NO by O₂ according to the stoichiometry of reaction (2):



The amount of NO_x that has been stored on the catalyst surface at the end of the NO pulse is near 0.58 mmol/g_{cat}. During the NO pulse, CO₂ evolution is also observed. This is due to the formation of nitrate species upon NO_x adsorption [16,19], that replace

Table 1

Experimental conditions of lean-rich cycles, TPD and TPO experiments. All the experiments have been carried out with a flow rate of 100 cc/min (at 273 K and 1 atm).

% (v/v)	Gas composition		TPD	TPO
	Lean-rich cycles			
	Lean phase	Rich phase		
O ₂	3	0	0	3
NO	0.1	0	0	0
H ₂	0	0.4	0	0
CO ₂	0.1	0.1	0.1	0.1
H ₂ O	1	1	1	1
He	Balance	Balance	Balance	Balance

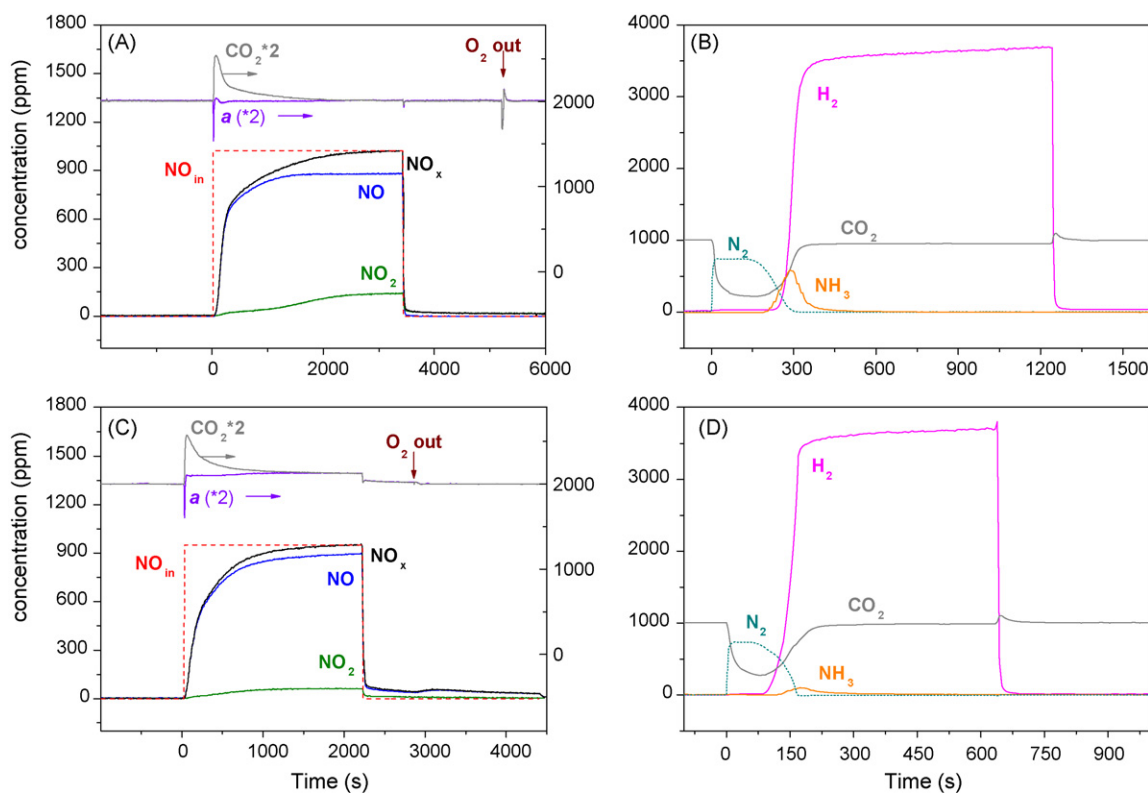
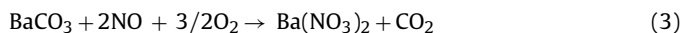


Fig. 1. Storage-reduction cycle performed at 623 K over PtBa/Al₂O₃ (A and B) and Pt-Ba/Al₂O₃-soot mixture (C and D). Trace a is the CO₂ production due to soot oxidation.

carbonates with release of CO₂ according to the stoichiometry of reaction (3),



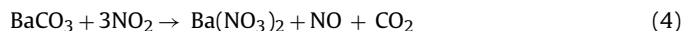
In fact upon subtracting half of the adsorbed NO concentration value (i.e. $1/2 (\text{NO}_{\text{IN}} - \text{NO}_{\text{OUT}})$) to the actual CO₂ concentration curve, a flat CO₂ trace is obtained (trace a of Fig. 1A).

Finally, upon NO shutoff near $t=3500$ s, a tail is observed in the NO and NO₂ concentrations due to the desorption of weakly adsorbed NO_x species (0.11 mmol NO_x/g_{cat} desorbed), whose release is favored by the decrease in the NO_x partial pressure. The net amount of NO_x stored before regeneration is hence is near 0.47 mmol NO_x/g_{cat}.

In presence of soot (Fig. 1C), the evolution of NO and NO₂ is qualitatively similar to those observed for the soot-free catalyst. Upon NO admission, the outlet NO concentration increases with time reaching a steady-state level after 2000 s. The formation of NO₂ is also observed, but in lower amount (60 ppm) if compared to the soot-free catalyst. The amount of adsorbed NO_x at the end of the pulse is in this case near to 0.41 mmol NO_x/g_{cat}, indicating a reduction in the storage capacity of the catalyst in presence of soot as also reported by Sullivan et al. [12].

A comparison of the amounts of NO_x stored vs. adsorption time for different soot loadings (curve a: soot-free catalyst; curve b: soot loading 2.9% (w/w); curve c: soot loading 8% (w/w)) is shown in Fig. 2. It clearly appears that the amount of soot present in the catalyst/soot mixture affects the NO_x storage behavior of the LNT system. In particular, the decrease of the soot loading (from curve c to curve a) leads to an increase of the NO_x storage capacity, in line with the results reported by Sullivan et al. [12]. These authors pointed out that the presence of soot is detrimental to the performance of a NO_x trap since soot itself offers another reaction route for the utilisation of NO₂ rather than the desired formation

of Ba(NO₃)₂ according to the stoichiometry:



As a matter of facts, upon comparing Fig. 1A and C, it is noted that the presence of soot affects the NO/NO₂ ratio. Indeed the NO/NO₂ value rises from a value near 6 for the soot-free catalyst sample to roughly 15 in presence of soot. The higher NO/NO₂ ratio measured in the presence of soot is due to the participation of NO₂ in soot oxidation, according to reaction (1).

In Fig. 1C, upon NO admission, CO₂ evolution is also observed above its background of 1000 ppm. The increase in the CO₂ outlet concentration results from two contributors: one is related to the decomposition of carbonates on the catalytic surface due to nitrates

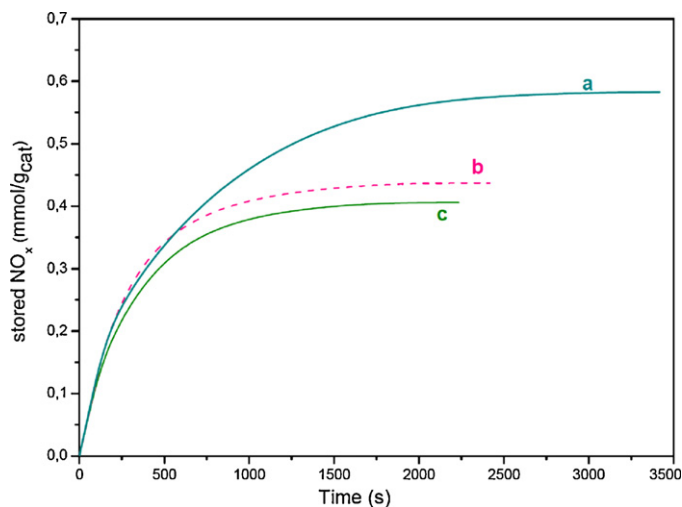


Fig. 2. Adsorbed NO_x vs. time over PtBa/Al₂O₃ for different soot loadings: (a) without soot, (b) 2.9% (w/w) soot and (c) 8% (w/w) soot.

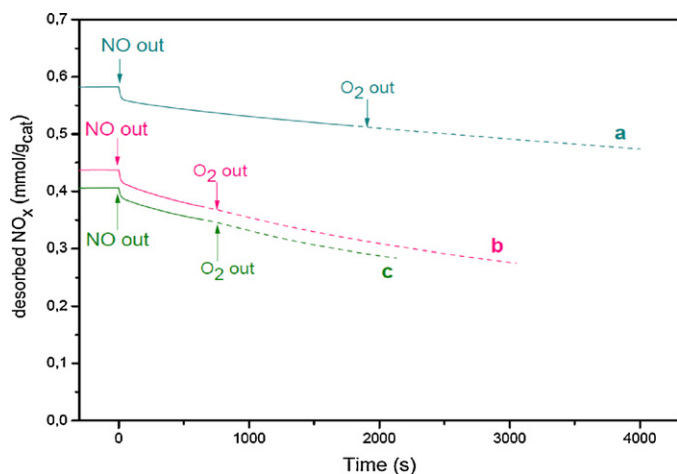


Fig. 3. Desorbed NO_x vs. time after NO_x storage over $\text{PtBa}/\text{Al}_2\text{O}_3$ for different soot loadings: (a) without soot, (b) 2.9% (w/w) soot and (c) 8% (w/w) soot.

formation (in line with reactions (3) and (4)), and the other is due to soot combustion. In order to evaluate the net CO_2 production due to the soot combustion, the contribution of the decomposition of the surface carbonates (reaction (3)) has been subtracted from the CO_2 outlet concentration trace; the obtained CO_2 net production curve is shown in Fig. 1C (trace a). During the lean phase roughly 4% of the soot initially present has been oxidized with a rate of approximately 1.08×10^{-5} mmol CO_2/s . Worth to note that at the investigated temperature soot combustion occurs only in the presence of NO. Besides, CO formation is not observed, possibly because the formed CO is further oxidized to CO_2 by O_2 on Pt sites.

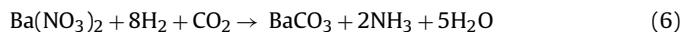
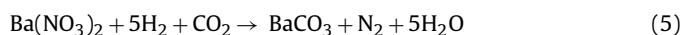
Upon NO shutoff, a release of NO and NO_2 takes place due to the desorption/decomposition of the NO_x species previously stored. Upon switching off the O_2 feed, additional NO_x are also desorbed. Both desorption contributions appear to be remarkable if compared to those observed in the case of the soot-free catalyst: this indicates that soot has a destabilizing effect on the nitrate species adsorbed onto the catalytic surface. The reasons for the destabilizing effect of soot on the stored nitrates are not yet fully understood; one can speculate that nitrates species, which are considered mobile on the catalytic surface [20], may directly interact with soot particles leading to its oxidation.

The changes in the amounts of adsorbed NO_x upon NO shutoff are reported in Fig. 3 as a function of time for different soot loadings (curve a: soot-free catalyst; curve b: soot loading 2.9% (w/w); curve c: soot loading 8% (w/w)). It appears that the higher the soot loading, the greater is the decrease of the amount of stored NO_x . After 2000 s, the total amounts of NO_x desorbed in the presence and in the absence of soot are near 0.12 mmol/ g_{cat} and 0.07 mmol/ g_{cat} , respectively; these values correspond to 29% and 12.4% of the NO_x adsorbed species present onto the catalytic surface at saturation. This clearly points out the lower stability of nitrates in presence of soot.

3.2. NO_x reduction phase

The reduction of the stored NO_x has been carried out at 623 K by admission of H_2 (rich phase, Table 1). The results are shown in Fig. 1B in terms of H_2 , CO_2 and N_2 , NH_3 outlet concentrations as a function of time in the case of the soot-free catalyst.

Upon H_2 admission ($t=0$ s), the H_2 outlet concentration profile shows a dead time during which it is completely consumed to give at first N_2 and NH_3 later on, according to the overall stoichiometry of reactions (5) and (6):



In line with the stoichiometry of reaction (5), upon admission of 4000 ppm H_2 the N_2 outlet concentration immediately increases to the level of 800 ppm; then NH_3 formation is observed in correspondence of the decrease of the N_2 trace, at the end of the reduction. Slightly after the NH_3 breakthrough the H_2 concentration trace increases up to the inlet concentration value. The integral amounts of the reduction products (0.21 mmol/ g_{cat} of N_2 and 0.07 mmol/ g_{cat} of NH_3) well correspond to H_2 consumption (1.46 mmol/ g_{cat}), according to the stoichiometry of reactions (5) and (6). N_2O is not observed among the reduction products, as indicated by GC analyses (detection limit near 10 ppm).

According to previous studies of our group [16,21] the reduction of stored nitrates by H_2 occurs via a two-steps molecular pathway which involves a first step leading to the formation of NH_3 , followed by the slower reaction of ammonia with residual nitrates to form N_2 :



The sum of reactions (6) and (7) accounts for the overall stoichiometry of reduction of nitrates with hydrogen to give N_2 (reaction (5)). Notably, the temporal evolution of reduction products, with nitrogen being detected at the reactor outlet first and ammonia later, is in line with the integral behavior of the catalytic bed [16,21]. In fact upon regeneration a hydrogen front travels along the catalyst bed. NH_3 is formed at the H_2 front upon reaction of H_2 with the stored NO_x ; the formed NH_3 then reacts with NO_x stored downstream the H_2 front, leading to the formation of N_2 . When the front reaches the end of the catalytic bed, there are no NO_x stored downstream and this leads to the evolution of ammonia, which follows that of N_2 .

During the reduction phase, a CO_2 uptake has also been observed due to the formation of carbonates onto the Ba sites on which NO_x were previously stored; finally, after NO_x reduction, the formation of small amounts of CO is also observed due to the occurrence of the inverse water gas shift (RWGS) reaction (8):



Calculation showed that the reaction is limited by thermodynamic constraints; the relevance of this reaction appears to be limited by the presence of water in the feed [16].

The reduction of the NO_x adsorbed species in the presence of soot (Fig. 1D) does not show significant differences with respect to the soot-free catalyst (compare Fig. 1B and D). Also in this case H_2 is immediately and completely consumed and at the beginning of the reduction phase only N_2 is observed among the products. After 150 s the concentration of nitrogen decreases to zero, that of H_2 progressively increases and NH_3 is observed at the reactor exit. In the presence of soot the amount of both N_2 and NH_3 which have been produced is lower if compared to the absence of soot, i.e. 0.11 mmol/ g_{cat} of N_2 and 0.02 mmol/ g_{cat} of NH_3 . This is related to the reduced NO_x storage capacity of the catalyst in presence of soot, as shown in Fig. 2 (curve c). However, the N_2 selectivity calculated in the presence of soot is very similar to that measured in its absence, i.e. 86% vs. 92%.

3.3. TPD experiments

In order to analyze the stability of adsorbed NO_x species in the absence and in the presence of soot, TPD experiments have been carried out (Table 1). Fig. 4A and B show the results obtained in terms of NO, NO_2 , and O_2 concentration traces vs. time on Pt–Ba/ Al_2O_3 in the absence and in the presence of soot, respectively.

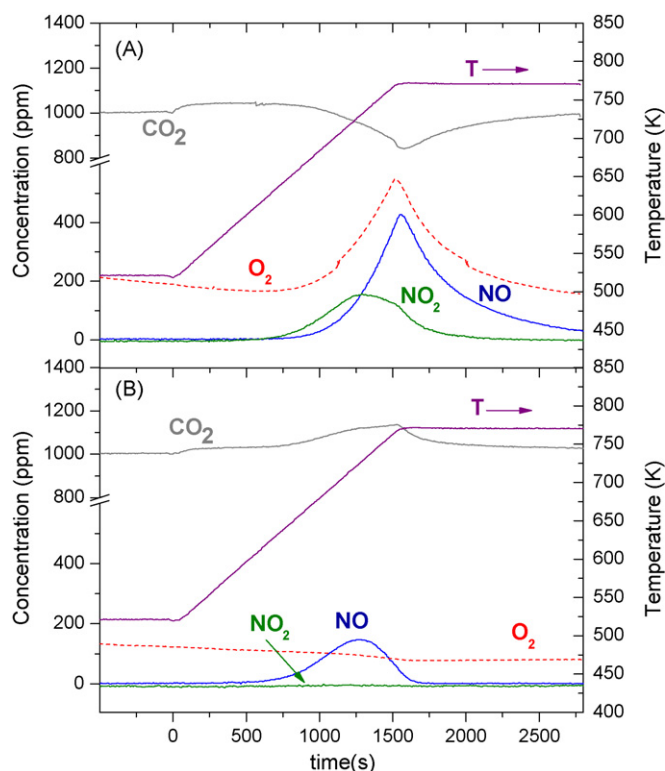
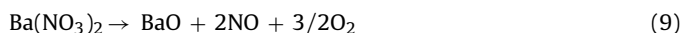


Fig. 4. TPD run after NO_x adsorption at 623 K over (A) PtBa/ Al_2O_3 catalyst and (B) PtBa/ Al_2O_3 catalyst–soot mixture.

In the case of the soot-free Pt–Ba/ Al_2O_3 catalyst (Fig. 4A), no desorption peaks were observed below the adsorption temperature (623 K). This is in line with previous results [16,22,23] showing that the adsorption temperature rules the thermal stability of the adsorbed NO_x species. Decomposition of nitrates occurs above the temperature of absorption and results in the initial evolution of NO_2 , followed by NO and O_2 . NO , O_2 , and NO_2 are likely produced through the following global reactions:



The process was not complete at temperatures as high as 773 K, corresponding to the maximum heating temperature; the catalyst was then kept at this temperature until desorption of nitrates was nearly complete (N-balance closes within 5.5%). After the TPD experiment a reducing treatment has been carried out with a stream of H_2 (4000 ppm in $\text{He} + \text{H}_2\text{O} + \text{CO}_2$) at 623 K to reduce the residual nitrates. During this treatment the formation of very small amounts of NH_3 (4.91×10^{-3} mmol/ g_{cat}) has been detected.

In correspondence with the nitrate decomposition, a decrease of the CO_2 signal is observed, from the inlet value (1000 ppm) to a minimum of 840 ppm. This is due to the adsorption of CO_2 on Ba forming BaCO_3 upon decomposition of Ba nitrates. Note that the amount of CO_2 adsorbed is lower than that expected from nitrates decomposition (according to reaction (3)), possibly due to the formation of Ba oxide and/or hydroxide, along with BaCO_3 .

TPD runs have also been performed in the presence of soot and results are shown in Fig. 4B. The decomposition onset of the stored NO_x is observed about at the same temperature of adsorption (623 K) for the reasons already discussed. The amounts of desorbed species is lower than that calculated in the absence of soot (0.11 mmol/ g_{cat} vs. 0.48 mmol/ g_{cat}), as consequence of the minor amounts of NO_x adsorbed onto the catalytic surface in the presence of soot, as already discussed. It is worth noticing that the distribu-

tion of desorbed products is different in the presence and in the absence of soot (compare Fig. 4A and B). Indeed in the presence of soot, NO represents the major decomposition product (Fig. 4B), and no detectable amounts of NO_2 or O_2 are observed. This suggests that in the presence of soot NO_2 and O_2 produced from the nitrates decomposition are readily consumed in the soot combustion. In line with the occurrence of soot oxidation, the CO_2 concentration trace shows an increase, as opposite to what observed in the absence of soot (Fig. 4A). This indicates that soot can be effectively oxidized at temperatures above the nitrate decomposition [10].

Finally, in Fig. 4B it appears that the nitrates decomposition is concluded at lower temperature (near 773 K) than in the absence of soot. This indicates that the presence of soot favors the decomposition of the NO_x adsorbed species, in line with isothermal experiments reported above (see Fig. 3).

3.4. TPO experiments

TPO experiments have been carried out (i) in the presence of adsorbed NO_x species only, (ii) in the presence of soot and (iii) in the presence of both soot and adsorbed NO_x species (Fig. 5A–C, respectively). In the presence of adsorbed NO_x species only (Fig. 5A) the decomposition of the stored NO_x was appreciable only above 623 K, with evolution of NO_2 and NO . Comparing these data with the results of TPD experiments discussed above (Fig. 4A), it appears that the products distribution is similar, with NO_2 and NO evolution above 623 K (O_2 evolution could not be detected in this case due to the high oxygen concentration in the feed stream). At the end of the heating ramp (773 K), the nitrate decomposition process was not complete; for this reason the temperature was kept at this value for several minutes. Like the TPD experiment, in correspondence of the NO_x desorption peak a decrease in the CO_2 concentration trace is observed, due to carbonates formation onto the catalytic surface. After the TPO experiment, the residual nitrates (roughly 18% of the initially stored NO_x) were removed by a reducing treatment with H_2 at 623 K.

In the presence of both nitrates and soot (Fig. 5B), the nitrates decomposition occurs at slightly lower temperatures than in the absence of soot. As already discussed in the case of the TPD run (Fig. 4B), no NO_2 is detected in this case at the reactor outlet due to its involvement in the soot oxidation. A significant CO_2 evolution is observed in this case, along with O_2 consumption. At 773 K the decomposition of nitrates is already complete and the subsequent reduction does not show any production of reduction products: these results are in agreement with those reported above in the case of the TPD experiment.

Finally, Fig. 5C shows the results of a TPO experiment carried out in the case of the soot–catalyst mixture, in the absence of pre-adsorbed nitrates. A minor CO_2 evolution is observed, produced by soot oxidation, along with a corresponding O_2 consumption. A comparison with the experiment carried out in the presence of surface nitrates (Fig. 5B) clearly points out that the presence of surface NO_x favors the soot oxidation, as pointed out by the greater amounts of evolved CO_2 in this case, 1.93 mmol/ g_{cat} vs. 1.36 mmol/ g_{cat} .

According to Kustov and Makkee [10] soot is oxidized in the presence of nitrates through two routes: oxidation with NO_2 and oxidation with oxygen. Oxidation with NO_2 occurs upon nitrate decomposition; according to the authors this mechanism may decrease the onset temperature for soot oxidation by some 100 K with respect to oxygen. The increase in the CO_2 concentration which is observed at the beginning of the TPO run carried out in the presence of adsorbed NO_x (compare Fig. 5B and C) may result from soot oxidation by NO_2 evolved upon decomposition of the stored nitrates. In fact only NO evolution is observed in this case upon nitrate decomposition, as opposite to what observed in the absence of soot (see Fig. 5A). This clearly indicates that NO_2 which

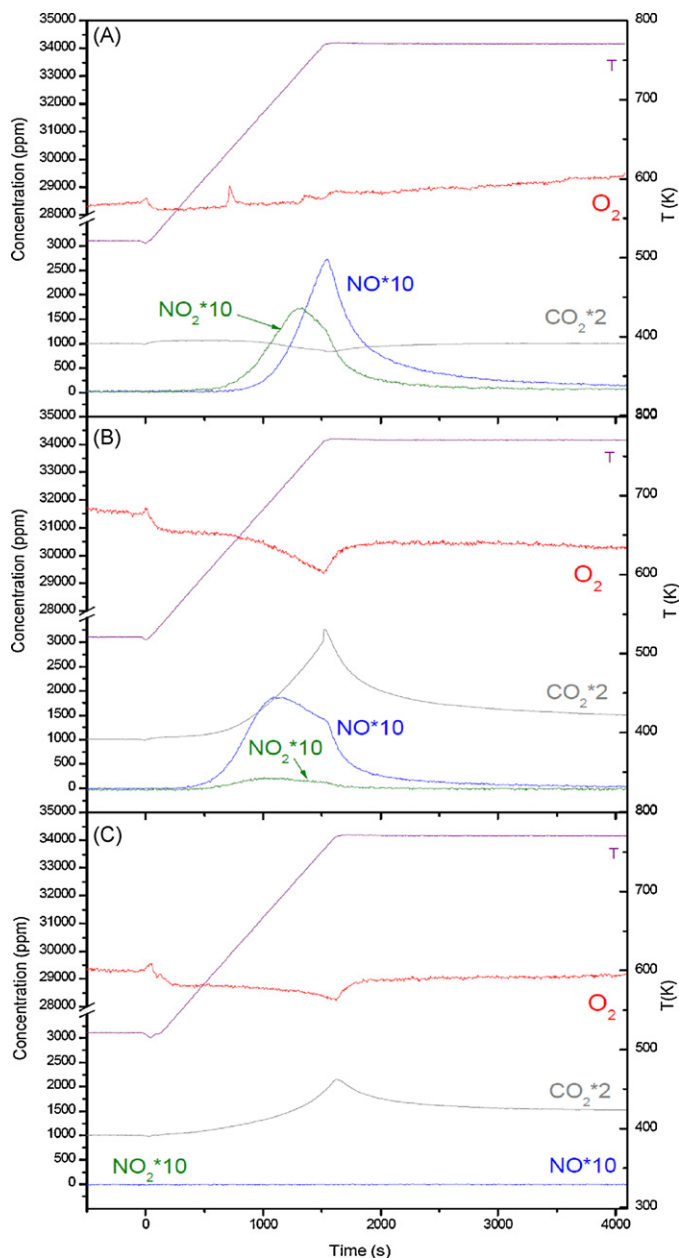


Fig. 5. TPO run after NO_x adsorption at 623 K over (A) $\text{PtBa}/\text{Al}_2\text{O}_3$ catalyst, (B) $\text{PtBa}/\text{Al}_2\text{O}_3$ catalyst-soot mixture and (C) $\text{PtBa}/\text{Al}_2\text{O}_3$ catalyst-soot mixture without nitrates pre-adsorbed onto the catalytic surface. CO_2 trace has been reported with an offset of 1000 ppm.

evolves upon decomposition of the stored nitrates, is involved in soot oxidation likely according to the stoichiometry of reaction (1). Notably, the increase in the CO_2 formation is much higher than that expected from the stoichiometry of reaction (1). This is due to the so-called “NO recycle”, i.e. to the oxidation of NO produced according to reaction (1) to NO_2 , catalyzed by Pt [24]. Besides, it has also been reported that the presence of NO_2 enhances soot oxidation by oxygen [25,26]. A specific role of the adsorbed NO_x species in the soot combustion cannot be ruled out, as also previously reported [6]. These mechanisms contribute to the significant increase in the soot oxidation which is observed when the soot combustion is carried out in the presence of adsorbed nitrates.

4. Conclusions

In this study the behavior of a model $\text{PtBa}/\text{Al}_2\text{O}_3$ model NSR catalyst in both the NO_x storage/reduction and soot oxidation has been addressed. It has been found that the presence of roughly 10% (w/w) of soot decreases by nearly 30% the NO_x storage capacity of the catalyst (0.58 mmol/g_{cat} vs. 0.41 mmol/g_{cat}). The presence of soot has also a destabilizing effect on the NO_x adsorbed species, likely due to the reaction between soot particles and the nitrate species which are mobile on the surface.

The behavior of the $\text{PtBa}/\text{Al}_2\text{O}_3$ catalyst sample in the reduction by H_2 of the stored nitrates has also been investigated, in the presence and in the absence of soot. It has been found that the presence of soot does not appreciably affect the features of the reduction of the stored NO_x , being in both cases N_2 the major reaction product along with minor amounts of NH_3 .

During the lean-rich cycles, and in particular during the storage of NO_x , soot oxidation takes place, pointed out by CO_2 evolution. Soot oxidation takes place only upon NO admission, and is almost negligible in the presence of O_2 only. As pointed out by TPD experiments, the stored NO_x participate in the soot oxidation upon release of NO_2 and O_2 which actively oxidize soot, although a direct participation of the stored NO_x in the oxidation of soot cannot be excluded. The participation of the adsorbed NO_x species in the soot oxidation has also been clearly pointed out by TPO experiments showing that the oxidation of soot is greatly enhanced by the presence of adsorbed NO_x species: indeed larger amounts of CO_2 are produced upon soot oxidation when the reaction is carried out in the presence of stored NO_x .

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